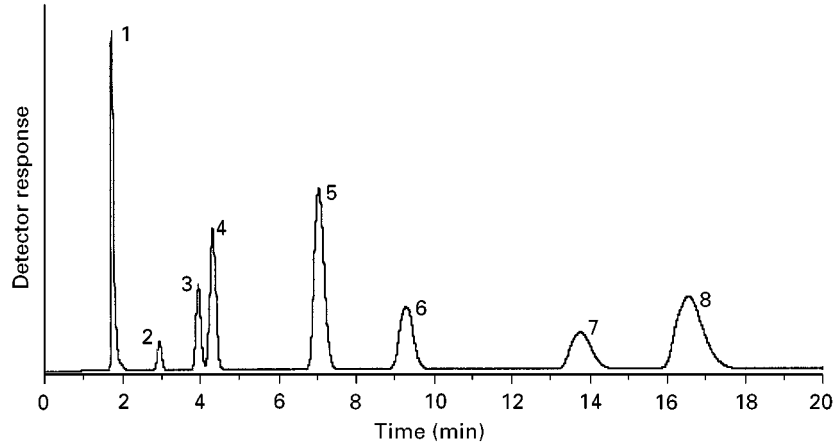


Figure 5 Functional group selectivity of PS-DVB column. Conditions: column, PLRP-S; temperature, 200°C. Solutes: 1, hydroquinone; 2, *p*-cyanophenol; 3, phenol; 4, *p*-methoxyphenol; 5, *p*-cresol; 6, *p*-bromophenol; 7, 3,5-xylenol; 8, 2,4-xylenol.

esters) which might be thought to be susceptible both to oxidation and to hydrolysis, have been separated without difficulty. One reason may be that, as the temperature is raised and the water becomes less polar, it also becomes a weaker hydrolysis agent.

See also: **II/Chromatography: Liquid:** Mechanisms: Reversed Phases; Nuclear Magnetic Resonance Detectors. **Extraction:** Supercritical Fluid Extraction. **III/Environmental Applications:** Pressurized Fluid Extraction. **Porous Polymers: Liquid Chromatography.**

Further Reading

Chienthavorn O and Smith RM (1999) Buffered superheated water as an eluent for reversed-phase high performance liquid chromatography. *Chromatographia* 50: 485–489.

Hawthorne SB, Yang Y and Miller DJ (1994) Extraction of organic pollutants from environmental solids with sub- and supercritical water. *Analytical Chemistry* 66: 2912.

Kuhlmann B, Arnett EM and Siskin M (1994) Classical organic reaction in pure superheated water. *Journal of Organic Chemistry* 59: 3098.

Miller DJ and Hawthorne SB (1997) Subcritical water chromatography with flame ionisation detection. *Analytical Chemistry* 69: 623.

Smith RM and Burgess RJ (1996) Superheated water – a clean eluent for reversed-phase high-performance liquid chromatography. *Analytical Communications* 33: 327.

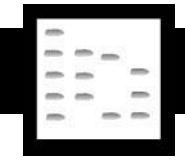
Smith RM and Burgess RJ (1997) Superheated water as an eluent for reversed-phase high-performance liquid chromatography. *Journal of Chromatography* 785: 49.

Smith RM, Chienthavorn O, Wilson ID, Wright B and Taylor SD (1999) Superheated heavy water as the eluent for HPLC-NMR and HPLC-NMR-MS. *Analytical Chemistry* 71: 4493–4497.

Yang Y, Bøwdt S, Hawthorne SB and Miller DJ (1995) Subcritical water extraction of polychlorinated biphenyls from soil and sediment. *Analytical Chemistry* 67: 4571.

DropBooks

SURFACTANTS



Chromatography

J. G. Lawrence, Unilever Research
Bebington, Merseyside, UK

Copyright © 2000 Academic Press

Introduction

'Surfactant' is a contraction of 'surface active agent'. It has come to be used interchangeably with detergent, particularly when applied to cleaning products such as fabric washing powders, soaps, hard-surface cleaners and the many other products used for cleaning in and around the home. Solutions of surfactants exhibit one or more of the properties of detergency, foaming, wetting, emulsifying, solubilizing and dispersing.

This article will deal with the main classes of surfactants used as commercial detergents, which are not single compounds but mixtures of compounds of the same general structure but having a range of alkyl chain lengths. Surfactants have the follow-

ing general properties:

- They are molecules composed of groups of opposing solubilities, typically an oil-soluble hydrocarbon chain and a water-soluble ionic group.
- They are soluble in at least one phase of a liquid system.
- They form oriented monolayers at phase interfaces.
- They form micelles (aggregates of molecules or ions) above a limiting concentration in solution.

Chromatographic separations are important in surfactant analysis for a number of reasons. The most important of these is based on their ability to separate both molecules of different, though similar, structures and molecules from within a structural family on the basis of carbon chain length, chain branching or positional isomer distribution. Many procedures for surfactant analysis give average values for the property determined. Two quite different examples are titrimetric determination of the active level of a surfactant which requires a value for the mean molecular weight of the surfactant to calculate the weight percent of active material and determination of the degree of ethoxylation of an alcohol or alkylphenol ethoxylate by proton nuclear magnetic resonance, which gives a value for the average degree of ethoxylation but no information on the ethoxamer distribution. Chromatographic techniques can supply the mean molecular weight to use with the titration and both the detailed ethoxamer and alkyl chain length distribution of the ethoxylate. Such detailed knowledge of molecular composition is required for full understanding of surfactants and their properties.

Other areas of surfactant analysis in which chromatographic techniques are used are determination of levels and composition of surfactants in products and in the environment, particularly in studying decomposition, and in studying the detailed composition of the surfactant itself including low levels of impurities or contaminants which may result from the manufacturing process. Legislative and consumer pressures for cleaner, safer, more environmentally friendly raw materials and products are resulting in such analyses becoming increasingly common.

In the following sections, the most common surfactants in the detergents and related industries and the chromatographic techniques (gas–liquid chromatography, high performance liquid chromatography, supercritical fluid chromatography, thin-layer chromatography, capillary electrophoresis) used in their analysis will be described. The examples have been chosen to illustrate the variety of sample preparation, separation and detection procedures which can be used.

Anionic Surfactants

Alkylbenzenesulfonates

Alkylbenzenesulfonates are the most common of the commercial anionic surfactants. Their general structure is *p*-alkylbenzenesulfonic acid, sodium salt (**Figure 1**) where the alkyl chain may range from C9 to C14 with the benzenesulfonate moiety attached in different proportions at each carbon atom from C2 to the central carbon of the chain. The carbon chain is essentially linear to permit biodegradation, though there is a minor usage of branched alkylbenzenesulfonates for specific applications.

Gas chromatography Gas chromatography (GC) of alkylbenzenesulfonates requires some pretreatment of the molecule to enable it to be volatilized. The most common pretreatments are desulfonation and derivatization. The following examples demonstrate a number of sample preparation and detection options:

- Desulfonation of alkylbenzenesulfonate with phosphoric acid to the corresponding linear alkylbenzene (LAB) followed by separation on a fused silica capillary column (**Figure 2**). This procedure enables both the alkyl chain lengths and the attachment points of the benzene ring along the chain to be determined.
- Desulfonated linear alkylbenzenesulfonate (LAS) or LAB can be prefractionated from complex detergent and environmental samples using argentation thin-layer chromatography (TLC), in which the TLC plate is coated with silver nitrate to modify the separation process. The separated spots are recovered from the plate and analysed using similar conditions to those in Figure 1. Electron impact mass spectrometry (EIMS) detection is used to give component identification.
- LAS and dialkyltetralinsulfonates are converted to their sulfonyl chlorides by reaction with phosphorus pentachloride and then to their trifluoroethyl derivatives by reaction with trifluoroethanol. These derivatives are separated using similar conditions to those described in Figure 2.

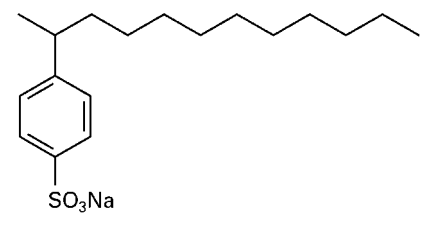
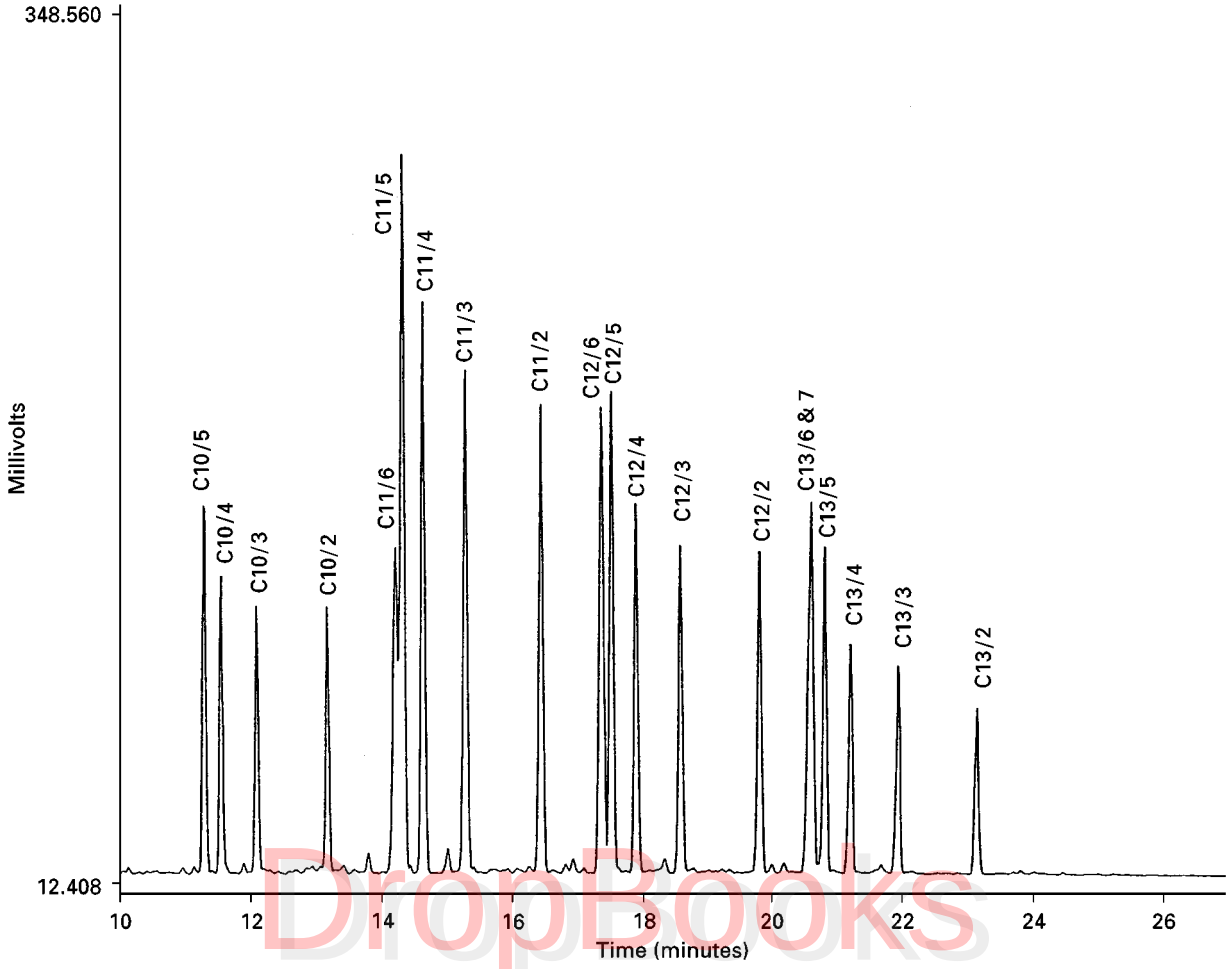


Figure 1 C12 2-phenylalkylbenzenesulfonate, sodium salt. Courtesy of RSC.



DropBooks

Figure 2 C10–C13 linear alkylbenzene. Column 25 m × 0.2 mm i.d. fused silica capillary of HP1 (0.33 μm film) programmed from 120°C to 240°C at 3°C per minute, final temperature held for 20 min, injector and detector at 275°C, FID, carrier helium at 1 mL min^{-1}, splitless injection. Courtesy of RSC.

- Aqueous solutions of LAS are shaken with tetrabutylammonium hydrogensulfate to form ion pairs. Injection of the ion-pair solution into a GC injection port at 300°C forms the butylsulfonate derivatives of the LAS which are separated on a HP-5 column (20 m × 0.2 mm i.d., 0.33 μm film) programmed from 110°C to 220°C at 10°C per minute then 300°C at 6°C per minute with a final 3-minute hold. Detection is by EIMS to give full spectral information.
- LAS is rapidly and efficiently converted to its methylsulfonate ester by derivatization with trimethoxyorthoacetate at room temperature and separated as in **Figure 3**.

High performance liquid chromatography The advantage of high performance liquid chromatography (HPLC) for the separation of LAS is that, in contrast to GC, sample preparation specifically to make the LAS compatible with HPLC is unnecessary. LAS can be determined by HPLC by a number of procedures of which examples to demonstrate different separation and detection conditions are given below.

The chain-length distribution of LAS can be determined on a column (300 × 3.9 mm) of μ-Bondapak C18 (10 μm) using a linear gradient from 70 : 30 acetonitrile–0.15 mol L^{-1} sodium perchlorate solution to 90 : 30 of the two solutions. UV photometric detection is at 230 nm. Peaks are eluted in order of increasing alkyl chain length.

The positional isomer distribution is determined using a column (250 × 4 mm i.d.) of Spherisorb ODS II (3 μm) with an isopropanol–water–acetonitrile gradient with 0.02 mol L^{-1} sodium perchlorate added and UV detection at 225 nm.

Both chain length and positional isomer distribution can be obtained using a Zorbax ODS column (250 × 4.6 mm i.d.) with a gradient from acetonitrile–water

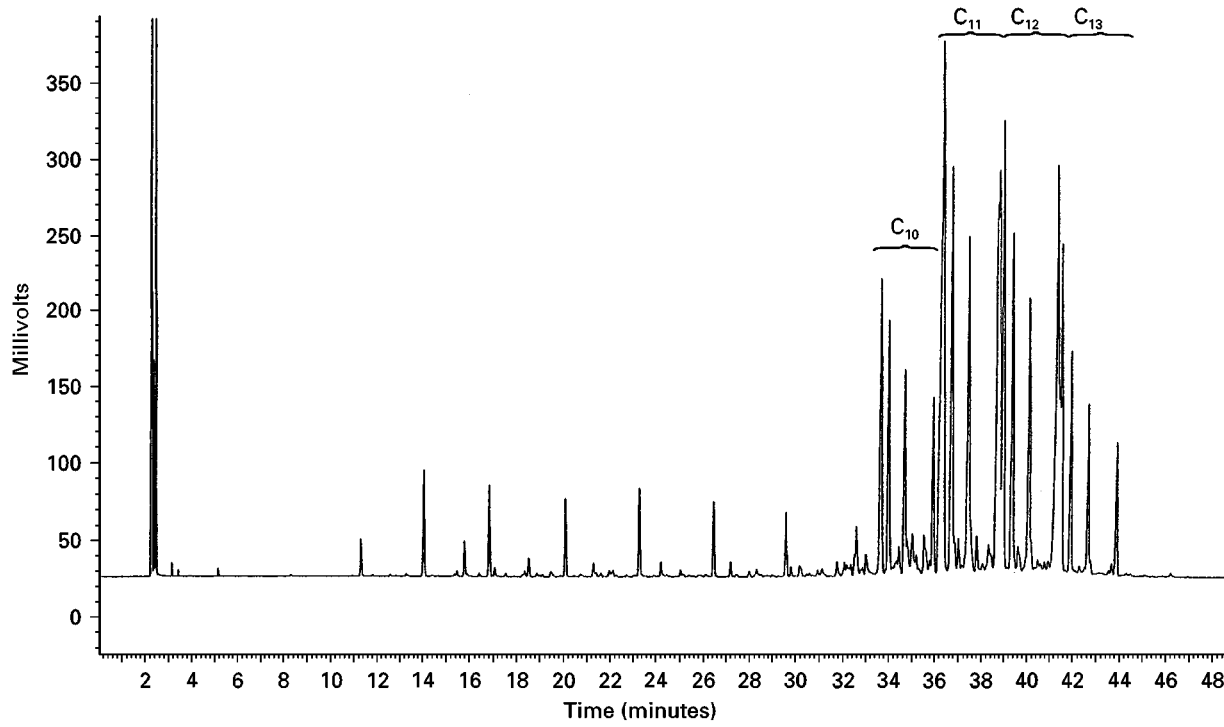


Figure 3 Chromatogram of methyl esters of C10–C13 linear alkylbenzene. Column 25 m × 0.2 mm i.d. fused silica capillary of HP1 (0.33 μm film) programmed from 120°C to 240°C at 3°C per minute, final temperature held 20 min, injector and detector at 275°C, FID, carrier helium at 1 mL min^{-1}, splitless injection. Courtesy of RSC.

(40 : 60) + 100 mmol L^{-1} sodium chloride to acetonitrile–water (60 : 40) with UV photometric detection at 225 nm.

Other separation techniques The analysis of LAS using a silica gel G layer (a standard TLC silica) impregnated with 10% ammonium sulfate and 2-methyl-4-pentanone–propyl alcohol–0.1 mol L^{-1} acetic acid–acetonitrile (20 : 6 : 1.6 : 1, v/v/v/v) and visualization by spraying with phosphomolybdic acid in ethanol followed by charring by heating has been described.

Supercritical fluid chromatography has been used for analysis of alkylbenzenesulfonates on a fused silica open tubular column (10 m × 0.53 or 0.25 mm i.d.) coated with a 0.1 or 0.2 μm film of SE54 with carbon dioxide as mobile phase and FID detection. The LAS is derivatized before analysis.

Capillary electrophoresis can be used for the separation of LAS by alkyl chain length. Conditions are a fused silica capillary (60 cm × 50 μm i.d., 40 cm to detector) with a buffer of acetonitrile–water (40 : 60), 3.0 mmol L^{-1} magnesium ion, pH 6.0, 10 mmol L^{-1} sodium acetate. Applied voltage is 30 kV and detection is by UV at 220 nm.

Alkyl Sulfates

Alkyl sulfates normally exist as a group of compounds with a range of alkyl chain lengths (**Figure 4**). They can be readily determined by GC following acid hydrolysis, recovery of the parent alcohols, and separation either as the alcohols or after conversion of the alcohols to their trimethylsilyl ether derivatives. Typical conditions are a 10 m × 0.53 mm i.d. column of methylsilicone phase programmed from 70°C to 240°C at 5°C per minute with helium as carrier and FID. The HPLC separation of alkyl sulfates by carbon chain length uses a column 25 cm × 4.6 mm i.d. ODS material with gradient elution from 60 to 30% aqueous acetonitrile containing 0.01 mol L^{-1} disodium hydrogenphosphate and 0.01 mol L^{-1} sodium nitrate. Detection is at 242 nm. This is an example of inverse photometric detection where nitrate in the mobile phase absorbs a constant level of radiation apart from when the level of nitrate is reduced by the presence of the non-absorbing alkyl sulfate anion. It is the reduced absorbance which is monitored.

Alkyl sulfates can be separated on a synthesized cross-linked amine-fluorocarbon polymer on silica column with 0.2 mmol L^{-1} naphthalenedisulfonate–35% acetonitrile mobile phase. Both indirect conductivity and indirect photometric detection can be used.

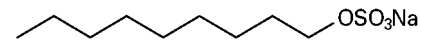


Figure 4 Sodium decyl sulfate. Courtesy of RSC.

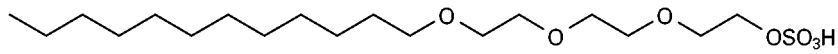


Figure 5 C12 alkyl 3-ethoxysulfate. Reproduced with permission from the American Chemical Society.

TLC separation of alkyl sulfates and alkyl ether sulfates using a silica gel layer with acetone–tetrahydrofuran (9 : 1, v/v) and visualization with Pinacryptol Yellow has been described.

Alkylethoxy Sulfates

Alkylethoxy sulfates (AES) have the general formula $CH_3(CH_2)_n(OCH_2CH_2)_mSO_4Na$ where n is commonly in the range 9 to 17 and mean values of m are in the range 2 to 20 (**Figure 5**). They are formed by reaction of alcohols with ethylene oxide to give a desired molar ratio of ethoxylate though in practice they are a broad distribution of ethoxylate ratios peaking at the desired mole ratio. The alcohol ethoxylate is subsequently sulfated.

The hydrophobe (alkyl chain) distribution of alkylethoxylated sulfates can be obtained through GC by reaction of the AES with 30% HBr in glacial acetic acid at 90°C overnight to give alkyl bromides followed by separation on a column (6 ft × $\frac{1}{4}$ in o.d.) of 10% OV-17 on Chromosorb W with temperature programming from 100°C to 250°C at 8°C per minute with helium as carrier gas and FID. AES can be analysed by HPLC on a 2.5 cm × 2 mm i.d. column of C18 reversed-phase material with a water–tetrahydrofuran gradient system. The detector is the evaporative light-scattering detector as the molecules being separated have no strong chromophore. There are a number of alternative gradient systems.

To obtain more detailed distributions by either GC or HPLC, the molecule can be desulfated and analysed as described below for ethoxylated alcohols.

Sulfonates

As for alkyl sulfates, alkylsulfonates exist in a range of alkyl chain lengths with the added complication that they can be primary, secondary or α-olefinsulfonates and also mono- and disulfonates with hydroxy and -ene substitution (**Figure 6**).

Alkylsulfonates are separated by HPLC on a synthesized cross-linked amine-fluorocarbon polymer or silica column with 0.2 mmol L^{-1} naphthalenedisulfonate–35% acetonitrile mobile phase. Both indirect conductivity and indirect photometric detection can be used.

Separation of positional isomers of alkylmonosulfonates is obtained using Hypersil ODS I phase with acetonitrile–water gradient and *N*-methylpyridinium chloride as visualization reagent for indirect photometric detection. Baseline separations are obtained.

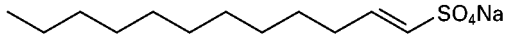


Figure 6 C13 α-olefin sulfonate, sodium salt.

As for LAS, aqueous solutions of secondary alkanesulfonates (SAS) can be shaken with tetrabutylammonium hydrogensulfate to form ion pairs. Injection of the ion-pair solution into a GC injection port at 300°C forms the butylsulfonate derivatives of the SAS which are separated using on an HP-5 column (20 m × 0.2 mm i.d., 0.33 μm film) programmed from 110°C to 220°C at 10°C per minute then 300°C at 6°C per minute with a final 3-minute hold. Detection is by EIMS to give full spectral information.

The separation of α-olefinsulfonates (AOS) into their hydroxy, alkene, and disulfonate isomers together with chain length information is achieved using a column (25 cm × 4.6 mm) of Zorbax TMS with a mobile phase of methanol–water (75 : 25, v/v) and refractive index detection. This separation has also been demonstrated at an operating temperature of 55°C.

An alternative column for separation of AOS by carbon chain and isomer is a Novapak Phenyl column (150 × 2 mm) with a mobile phase of 70 : 20 : 10 10 mmol L^{-1} ammonium acetate–acetonitrile–tetrahydrofuran (THF) at 0.2 mL min^{-1} with full-scan MS detection to confirm peak identification. Supercritical fluid chromatography has been used for analysis of alkylsulfonates on a fused silica open tubular column (10 m × 0.53 or 0.25 mm i.d.) coated with 0.1 or 0.2 μm SE54 with carbon dioxide as mobile phase and FID detection. The sulfonates are derivatized as described above for LAS before analysis. Capillary electrophoresis can be used to separate C4 to C12 alkanesulfonates by alkyl chain length. Conditions are a fused silica capillary (60 cm × 50 μm i.d., 40 cm to detector) with a buffer of aqueous pH 7.0, 1.0 mmol L^{-1} magnesium ion, 5.0 mmol L^{-1} phosphate, 5.0 mmol L^{-1} salicylate solution. Applied voltage is 30 kV, and indirect photometric detection is at 230 nm.

Other Anionics

Sodium salts of alkyl (C10–C14) sulfosuccinates are separated on a 250 × 4.6 mm i.d. column of 10 μm Nucleosil C8 with aqueous 0.01 mol L^{-1} tetrabutylammonium hydrogensulfate–methanol (23 : 77) at pH 3 as mobile phase with refractive index detection.

The separation of sodium isethionate from its alkyl isethionate ester on a Vydac 302 IC column with

DropBooks

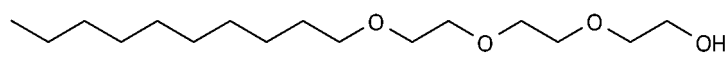


Figure 7 C10 alkyl 3-ethoxylate.

methanol–20 mol L^{-1} phthalic acid–water (3 : 5 : 12) and conductivity detection has been described.

Nonionic Surfactants

The two most common nonionic surfactants are ethoxylated alcohols and ethoxylated alkylphenols (**Figure 7**). Synthesis of alkyl ethoxylates is described above under AES. Alkylphenyl ethoxylates are synthesized similarly but with the added structural feature that the phenyl ring is attached at different carbon atoms along the alkyl chain. The alkyl chain is commonly nine carbon atoms.

Ethoxylated alcohols and alkylphenols can be separated by GC on a fused silica capillary column (30 m × 0.25 mm; 0.25 μm film) of SE-54 using helium as carrier gas and EI or CI (chemical ionization) (methane) MS detection. Temperature programming is from 70°C (1 min) to 300°C (10 min hold) at 3°C per minute. Ethoxylates up to 6 EO units are detected.

Separation of alkylphenyl ethoxylates and alkyl ethoxylates on an aluminium-clad fused silica column (10 m × 0.53 mm i.d.) of OV-1 with helium as carrier gas, FID, and temperature programming to 325°C has been demonstrated. The hydrophobe distribution can be obtained via reaction to alkyl bromides as described above for AES.

Silylation of alcohol ethoxylates to their trimethylsilyl ether derivatives, when combined with temperature-programmed GC using a non-polar methylsilicone column, gives an extremely complex pattern of peaks (**Figure 8**).

HPLC analysis of alkyl ethoxylates is made complicated by the lack of a strong UV chromophore. Derivatization to introduce a chromophore is an option. Reaction to form phenyl isocyanate derivatives which can then be detected by UV after separation on a μ-Bondapak C18 column according to alkyl chain length or on a μ-Bondapak amine column according to degree of ethoxylation. The evaporative light-scattering detector reduces the need for derivatization for HPLC. Separation by ethoxamer is shown in **Figure 9**.

Alkylphenol ethoxylates can be readily detected by UV. Columns and separation conditions are similar

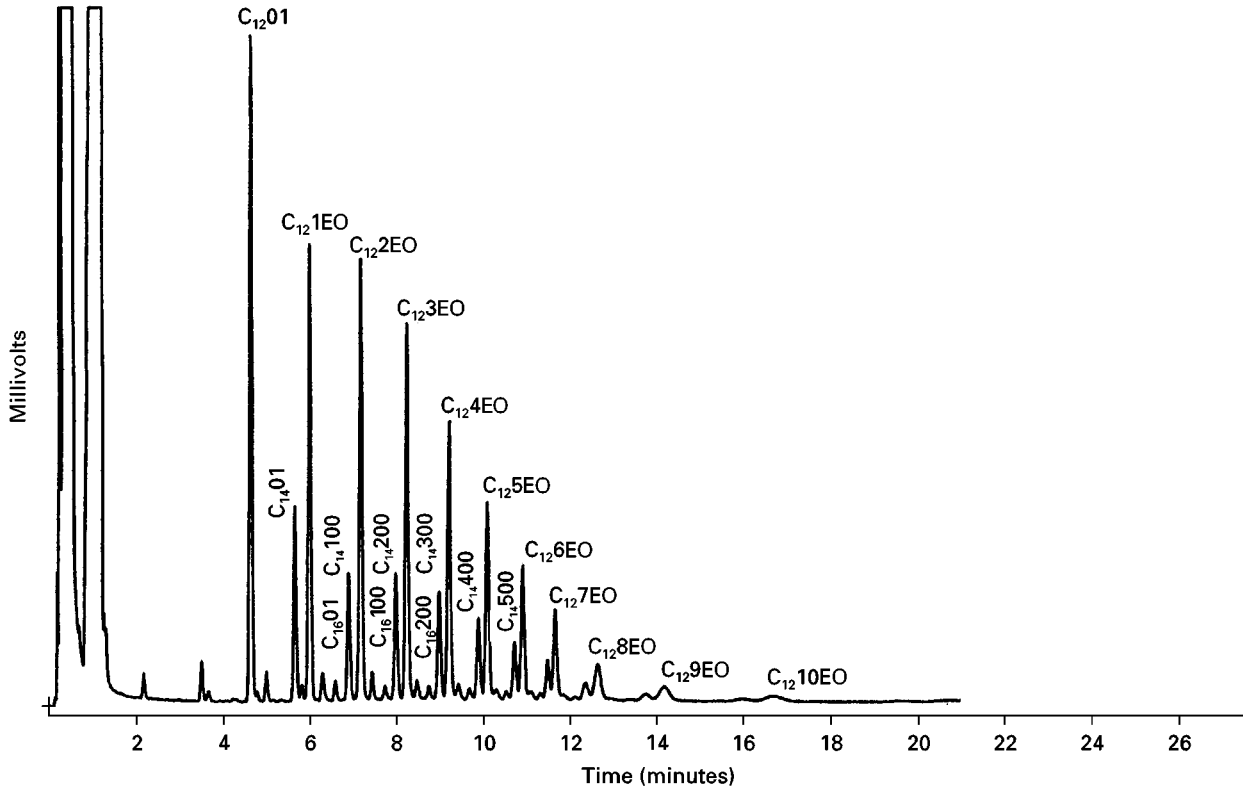
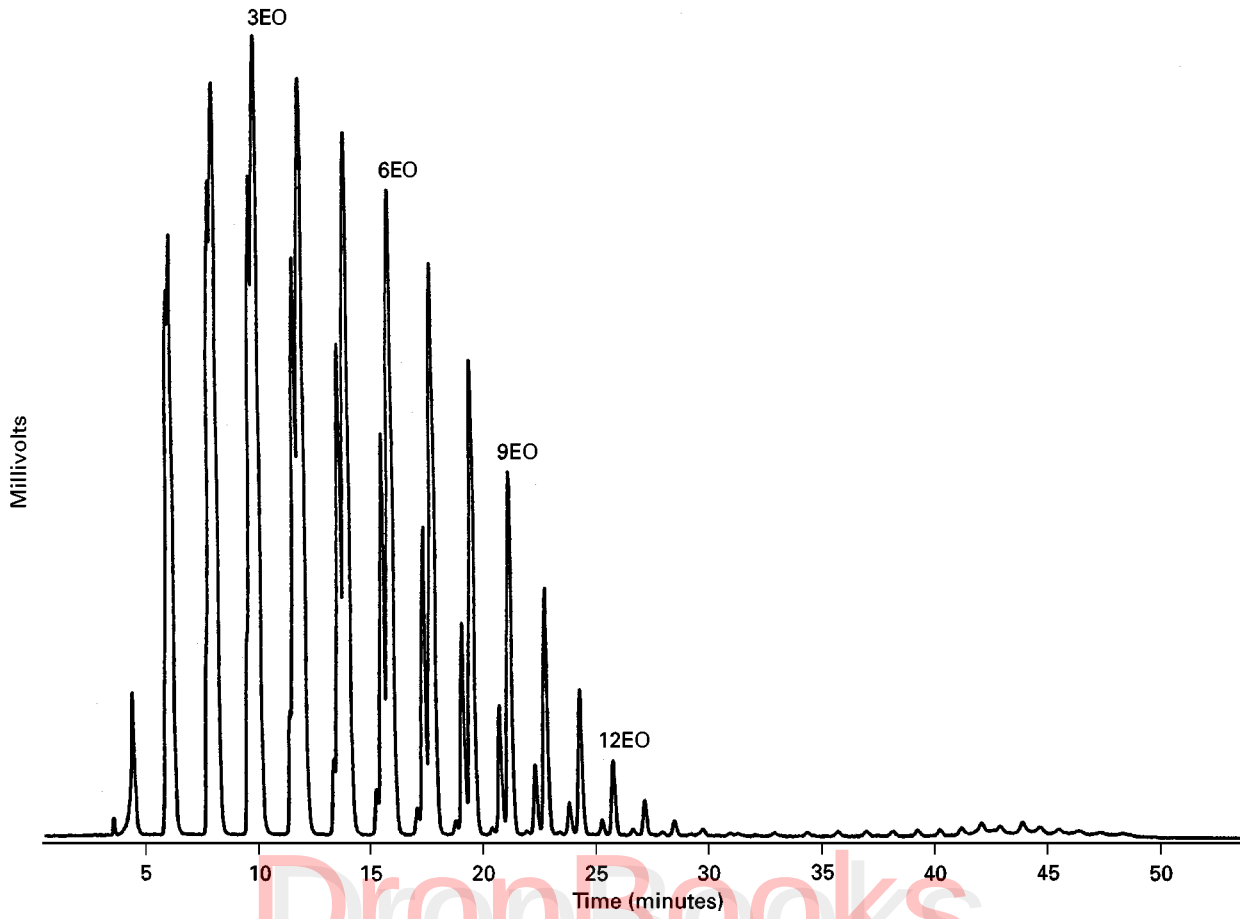


Figure 8 Separation of C12/C14/C16 3 EO alkyl ethoxylate as trimethylsilyl ethers. Column 10 m × 0.53 mm i.d. methylsilicone (1.0 μm film) programmed from 70°C to 240°C at 10°C minute, injector and detector 270°C, carrier helium at 15 mL min^{-1}, FID.



DropBooks

Figure 9 HPLC of C12/C14/C16 alkyl 3 EO ethoxylate. Column 250 × 4 mm i.d. Nucleosil 50 silica. Linear gradient: ethyl acetate–water (99 : 1, v/v) to acetone–water (90 : 10, v/v) over 60 min. Evaporative light-scattering detector.

to those for alcohol ethoxylates. Ethoxamer distribution can be determined on a LiChrosorb amine column (250 × 4.6 mm i.d.) with a hexane–isopropanol to aqueous isopropanol gradient system and UV detection at 277 nm.

Separation of ethoxylated fatty acids is obtained using a column (250 × 4.6 mm i.d.) of Nucleosil DIOL with hexane–isopropanol–water–acetic acid (105 : 95 : 10 : 1, v/v).

TLC can also be sued for the determination of nonionic surfactants using a silanized silica gel GF254 layer with aqueous 80% methanol as developing solvent and a scanning densitometer at 525 nm for detection.

Alkylphenyl ethoxylates may be analysed using a Kieselgel F60 layer with chloroform–methanol as developing solvent. IR detection is feasible with such systems.

Supercritical fluid chromatography (SFC) has been extensively applied to analysis of alcohol ethoxylates. Examples are separation of ethoxylated alcohols on a 20 m × 0.1 mm i.d. column of poly(dimethylsiloxane) with density programmed carbon dioxide at 100°C as mobile phase and FID. Response factor corrections are required for quantitative analysis. SFC can be used to determine alkyl chain distributions of ethoxylated alcohols after reaction with 50% HBr in glacial acetic acid to give their alkyl bromides.

An alternative to FID detection for SFC analysis of these molecules is evaporative light-scattering detection.

Cationic Surfactants

Cationic surfactants are generally based on a quaternary ammonium structure with a number of long (>C10) alkyl chains attached either directly to the nitrogen atom or through an ester linkage (**Figure 10**).

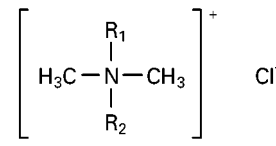


Figure 10 Dialkyldimethylammonium chloride. R_1 and R_2 are typically based on hardened tallow.

As cationics are nonvolatile, the contribution which GC can make to their analysis is in determination of their alkyl substitution. This is achieved by a degradation reaction. Alkyltrimethylammonium and dialkyldimethylammonium cationics are converted by Hoffmann degradation to their alk-1-enes by heating on a water bath for 30 min with potassium t-butoxide in benzene–DMSO (4 : 1). After extraction and clean-up, the alkenes are separated on a glass column (2 m × 3 mm i.d.) of 5% SE-30 on Chromosorb W AW-DMCS (80–100 mesh) temperature programmed from 160°C to 270°C at 6°C per minute with nitrogen as carrier gas and FID.

Alkyl chain distribution can also be obtained by thermal decomposition in the chromatograph injection port followed by separation on a 1 m × 2 mm i.d. column packed with 8% Carbowax 20M (KOH treated) on acid-washed Chromosorb W (80–100 mesh) and programmed from 70°C to 210°C at 8°C per minute with nitrogen as carrier gas and FID.

The chain-length distribution for cationics containing ester linkages is obtained by alkaline hydrolysis followed by extraction of the resulting fatty acids and conversion of the acids to their methyl esters. (See below for separation conditions.)

Cationic surfactants are more amenable to HPLC than to GC analysis as HPLC can analyse the intact molecule. The separation of mono-, di-, and trialkyl methylammonium quaternaries uses a column 250 × 4.6 mm of 5 μm RSil Polyphenol with guard column, a mobile phase gradient from 90 hexane–10 THF–methanol to 10 : 90, both solvents containing 5 mmol L^{-1} trifluoroacetic acid, and evaporative light-scattering detection.

Cationics of the structure alkylamidopropyl-*N*-(2,3-dihydroxy)-*N*,*N*-dimethylammonium chloride have been analysed on a column (150 × 4 mm i.d.) of μ-Bondapak CN with water–acetonitrile–THF (57 : 42 : 1, v/v) containing 0.1% trifluoroacetic acid as mobile phase and differential refractive index detection. Quantification is with an external standard and the method has also been applied to cosmetic as well as detergent products. Cationics of the structure difatty acid ester of 2,3-dihydroxypropyltrimethylammnoium chloride can be separated into mono- and di-esters on a Partisil PAC column 250 × 4.6 mm i.d. with chloroform–methanol–acetic acid (94 : 6 : 0.1, v/v) as mobile phase and refractive index detection.

The separation of imidazoline type cationics on a column (150 × 4.6 mm i.d.) of 3 μm Develosil ODS-3 with 0.1 mol L^{-1} sodium perchlorate in methanol–acetonitrile–deionized water (60 : 60 : 5, v/v) as mobile phase and UV detection at 240 nm has been demonstrated. This procedure gives separation of different chain-length alkyl substitution.

A final example of separation of dialkyldimethylammonium quaternaries on a column of 5 μm PLRP-S with a mobile phase of 5 mmol L^{-1} methanesulfonic acid in 70% acetonitrile uses post-column ion suppression and atmospheric pressure ionization mass spectrometry for component identification. TLC can be used to separate and compare cationics of the dialkyldimethylammonium, fatty acid esters of 2,3-dihydroxypropyltrimethylammonium, and fatty acid esters based on methyltriethanolamine quaternaries on a single plate. Separations are by numbers of substituent groups and the different structures are also separated. Conditions are Merck HPTLC Silica HF_{254} with a developing solvent chloroform–methanol–acetic acid–water (72 : 20 : 5 : 3, v/v). Visualization can be with iodoplatinate spray reagent.

Soap

Soap, the sodium salt of fatty acids in the chain length range C10 to C18 (**Figure 11**) is analysed by protonation of the salts to their acids and derivatization of the acids with boron trifluoride–methanol to give fatty acid methyl esters. A wide range of stationary phases and conditions have been used for the separation (**Figure 12**). The fatty acids obtained from soap can be analysed by HPLC without derivatization using a column (150 × 4 mm i.d.) of 5 μm Hitachi Gel 3056 at 50°C with methanol–5 mmol L^{-1} tetrabutylammonium phosphate (3 : 1, v/v) at pH 7.5 with conductivity detection.

Betaines

Betaines are amphoterics. The two most common types are alkylbetaines and alkylamidopropylbetaines. The alkyl moiety of the latter is generally based on coconut fatty acids.

Separation by chain length of both types of betaine is obtained on a cation-exchange column, Nucleosil 100-5 SA, 5 μm, 250 × 4 mm i.d., with a mobile phase of 70% acetonitrile–30% 0.05 mol L^{-1} lithium hydroxide in water adjusted to pH 1.6 with phosphoric acid (v/v). A column temperature of 40°C is used together with diode array detection at 210 nm.

Contaminants

Common contaminants in commercial surfactants are ethylene oxide, 1,4-dioxane, sultones and dialkyltetralins.

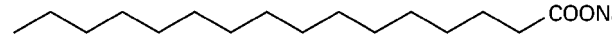


Figure 11 Sodium salt of palmitic acid.

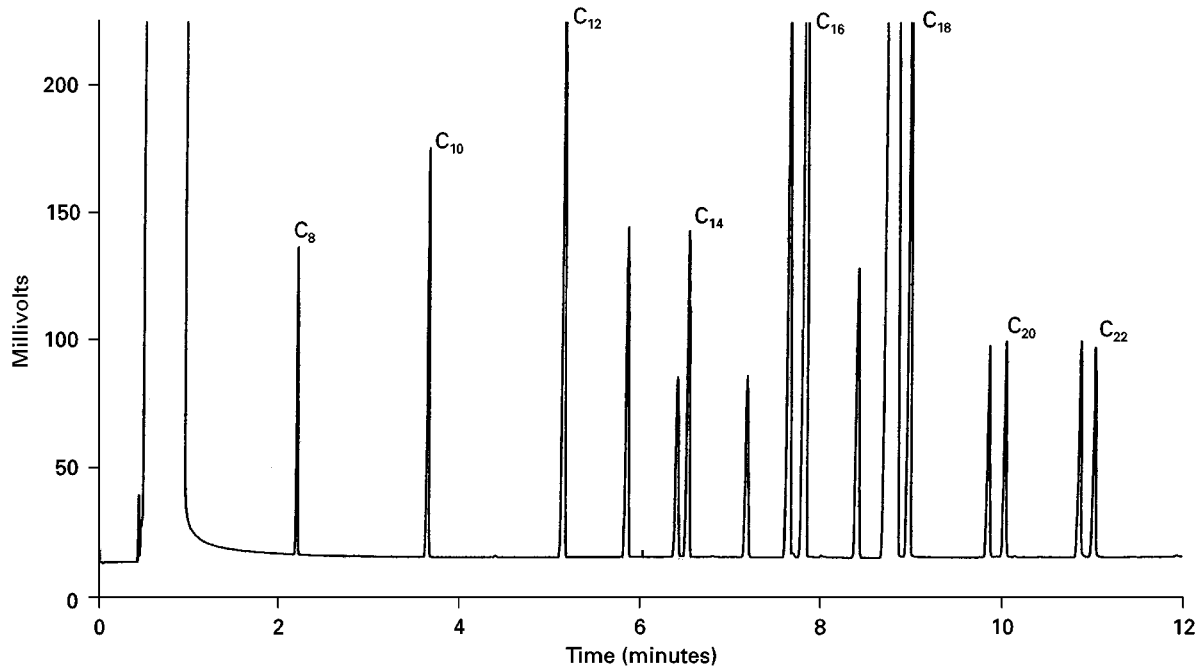


Figure 12 C8 to C22 fatty acid methyl esters. Column: Chrompack CPSIL5, 10 m × 0.32 mm i.d., film 0.12 μm, temperature programme 50°C to 200°C at 15°C per minute. Carrier helium at 1.5 mL per minute, FID, cool-on-column injection.

Ethylene oxide is used for ethoxylation of alcohols and alkylphenols. Levels of unreacted ethylene oxide are defined and must not be exceeded in the finished raw material.

Ethylene oxide in alcohol ethoxylates is determined by equilibrium headspace analysis. An aliquot of the vapour is analysed on a column (8 ft × 0.125 in) of Chromosorb 102 (80–100 mesh) (a gas–solid phase) programmed from 120°C (5 min) to 190°C (10 min) at 8°C per minute, with helium as carrier gas and FID. A detection limit of 1 $\mu g\,g^{-1}$ is achieved. An alternative column, also used for ethylene oxide in AES, is 3 m × 1.8 mm i.d. 0.8% THEED/Carbopack C (80–100 mesh).

For improved quantification, both methods can be adapted to a method of standard additions.

1,4-Dioxane is a by-product of the sulfation of alcohol ethoxylates. The industry standard method is equilibrium headspace GC and involves sample preparation using the method of standard additions for quantification. There is some flexibility as to whether capillary or packed columns are used and the actual phase required.

An alternative approach describes the use of a totally deuterated 1,4-dioxane analogue with isotope dilution and MS detection to minimize matrix effects. The separation is carried out on a 60 m × 0.32 mm i.d. column of Supelcowax 10, temperature programmed from 50°C (2 min) to 100°C at 5°C per minute.

An HPLC approach for 1,4-dioxane in alkylether sulfates is a column (250 × 4.6 mm i.d.) of 5 μm LiChrospher C-8 with an aqueous acetonitrile gradient and UV detection at 200 nm. An external calibration curve is used for quantification.

1,3- and other sultones occur as by-products of the formation of α-olefin sulfonates. Certain sultones are potent sensitizers and must be controlled. 1,3-Sultones are determined in α-olefin sulfonates by extraction with diethyl ether, trapping from a silica column, and GC on a column (1 m × 3 mm) of 2% DEGS on Chromosorb W AW-DMCS (60–80 mesh) at 220°C with helium as carrier and flame photometric (sulfur mode) detection.

Alternatively, detection limits down to 0.2 $ng\,g^{-1}$ can be obtained with negative chemical ionization MS with methane as reagent gas. 1,3-Sultones can also be determined by HPLC following extraction from α-olefin sulfonate and separation on a column (200 × 4.6 mm i.d.) of 5 μm CPS Hypersil with hexane–ethyl acetate (90 : 10, v/v) as mobile phase and differential refractive index detection. Quantification is by external standard.

Dialkyltetralins occur in linear alkyl benzene, the precursor of LAS. Again, there are set limits as to permissible levels. They are determined on a column (250 × 4 mm i.d.) of 5 μm Lichrosorb Si60 with dry iso-octane as mobile phase and UV detection at 254 nm. A reference standard is available from ECOSOL to calibrate the method.

DropBooks

Future Developments

As has been described above, there are many alternative approaches to the chromatographic analysis of commercial surfactants. The approach to be used for any analysis may be determined by a number of factors, the information required, the equipment available, the time available to carry out the analysis. As we move into the twenty-first century, there will be a trend towards faster analysis and analysis requiring less sample handling. Automation will increase, requiring less and less skilful human input. Data handling will become faster and more intelligent in order to deal with greater volumes of data generated in shorter times. Use of new separation techniques will be investigated, particularly electro-driven techniques and some will replace existing techniques for certain analyses. Overall, separation systems will become smaller with advantages of lower solvent and carrier gas use, less use of laboratory space, and with increased portability to permit use away from the laboratory.

See also: **II/Chromatography: Gas:** Detectors: Selective. **Chromatography: Liquid:** Derivatization; Detectors: Evaporative Light Scattering; Ion Pair Liquid Chromatography. **Chromatography: Thin-Layer (Planar):** Densitometry and Image Analysis; Layers. **III/Detergent Formulations: Ion Exchange. Surfactants:** Liquid Chromatography. **Thin-Layer Chromatography-Vibration Spectroscopy.**

Further Reading

Cullum DC (ed.) (1994) *Introduction to Surfactant Analysis*. Glasgow: Blackie A & P.

Kirk-Othmer (1997) *Encyclopedia of Chemical Technology. Surfactants*, 4th edn. New York: John Wiley.

Spitz L (ed.) (1996) *Soaps and Detergents. A Theoretical and Practical Review*. AOCS Press.

Liquid Chromatography

T. M. Schmitt, BASF Corporation, Wyandotte, MI, USA

Copyright © 2000 Academic Press

Introduction

Liquid chromatography (LC) is very useful for the characterization of individual surfactants. Most commercial surfactants are mixtures of members of homologous series, and LC is capable of defining these mixtures according to their homologue distribution, indicating, for example, alkyl chain length or degree of polymerization. LC is also the preferred technique for the quantitative determination of many surfactants, especially ionic surfactants in mixtures. The utility of LC stems from the properties of surfactants – these compounds have good solubility in the usual LC mobile phases and possess diverse chemical functionality, but at the same time they are not volatile enough for ready analysis by alternative technologies such as gas chromatography (GC) or simple mass spectrometry (MS). The structures of common surfactants are given in **Table 1**.

Surfactants are usually analysed in LC systems containing a substantial percentage of organic solvent so as to inhibit micelle formation. The presence of micelles will confound LC analysis.

Formulations and Mixtures of Surfactants

LC is used for quality control of formulations such as cleaning compounds and pharmaceutical preparations. LC is often the easiest and most specific method for determining surfactant concentration in a well-understood mixture. On the other hand, LC is not often useful for analysis of unknown formulations unless MS detection is available. This is because of the limited separation range of any single LC system.

Sometimes, especially in quality control where there are no unknown components, no preliminary sample work-up is necessary. This is particularly true of ionic surfactants. More often, especially for nonionics, a gross separation of the surfactants from the matrix is required. This can be accomplished by solvent extraction of the dried solids or by liquid–liquid extraction or solid-phase extraction (SPE) of an aqueous solution.

Alkylarylsulfonates and alkylphenol ethoxylates can be determined with a minimum of sample work-up because of the availability of a specific detection method, fluorescence, to distinguish them from other surfactant and nonsurfactant compounds that may also be present. For the very common mixtures of anionic and nonionic surfactants, ion exchange chromatography systems result in nonionic surfactants eluting prior to anionics, while reversed-phase systems result in the nonionics being retained longer than anionics.

Environmental Analysis

LC is widely applied in environmental analysis, but it is not used for routine monitoring of effluents, except by industry for the analysis of specific process streams